Journal of Cleaner Production 172 (2018) 1232–1242

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Carbon dioxide and ethanol from sugarcane biorefinery as renewable feedstocks to environment-oriented integrated chemical plants.

Camila Fernandes Ribeiro Machado [a], Ofélia de Queiroz Fernandes Araújo [a], José Luiz de Medeiros [a], Rita Maria de Brito Alves [b, *]

[a] Federal University of Rio de Janeiro, Rio de Janeiro, Brazil
[b] Universidade de São Paulo, São Paulo, Brazil

ARTICLE INFO

Article history:
Received 21 January 2017
Received in revised form
17 October 2017
Accepted 18 October 2017
Available online 24 October 2017

Keywords:
Chemical process integration
Carbon dioxide utilization
Green engineering
Carbon dioxide chemistry
Process simulation
Sustainability analysis

ABSTRACT

The chemical industry share of environmental impacts derives predominantly from the use of non-renewable feedstocks and inefficient use of mass and energy, resulting in atmospheric emissions, especially carbon dioxide, which is the main cause of global warming and climate change and expressive generation of wastes. Rather than treating carbon dioxide as waste, it can be regarded as an alternative chemical feedstock for synthesis of fuels and chemicals. Using carbon dioxide as a renewable and environment-friendly source of carbon is one of the most attractive solutions to reduce our dependence on petrochemicals. This work evaluates the utilization of carbon dioxide as feedstock to the production of chemicals arranged in an industrial eco-pole to reduce environmental impacts of a sugarcane biorefinery. This environment-oriented chemical complex, the Eco-Pole, aims to increase the sustainability of the sugarcane bioethanol industry located nearby the complex using carbon dioxide produced in the sugarcane fermentation and bioethanol itself as feedstocks. The Eco-Pole benefits from the nearly pure carbon dioxide to produce chemicals traditionally derived from fossil raw materials, namely methanol, propylene, ethylene, ethylene oxide, propylene oxide, ethylene carbonate, propylene carbonate and dimethyl carbonate. Process simulation using Aspen HYSYS® is used to compute mass and energy balances to support the calculation of quantitative performance indexes (e.g., net carbon dioxide emissions, energy intensity and water intensity) to compare efficiency of individual process and arranged in the Eco-Pole. The propylene oxide plant shows best individual performance, while the worst performance occurs for the ethylene plant. A multi-criteria analysis ranking sustainability performance points to the dimethyl carbonate plant as the most sustainable and the propylene plant as the poorest performer. The Eco-Pole cash flow presents a deficient economic performance, but with a tendency to profitability. Nevertheless, Eco-Pole shows satisfactory performance regarding the raw material and energy consumption indexes. Moreover, the carbon dioxide emission per Eco-Pole products is relatively low.
© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

In recent years, environmental issues have been in the spotlight, with the move to reduce greenhouse gas emissions, driving the development of clean technologies targeting simultaneously environmental and economic goals (Anastas and Eghbali, 2010). Aligned with this movement, Anastas and Warner (1998) proposed 12 guidelines to make chemistry greener - the concept of green chemistry - to lead progresses in catalysis, safer and environmentally benign solvents, and use of renewable feedstocks (Anastas and Kirchhoff, 2002). These guidelines were further transported to green engineering principles (Anastas and Zimmerman, 2003), applicable to early conception stages of processes and products, and green energy engineering (Oncel, 2017), promoting renewable energy alternatives and efficient energy management. The common point among the proposed principles is to create engineering solutions and technologies that offset the production of waste.

Process and product design should integrate and interconnect available energy and materials flows (Anastas and Zimmerman, 2003), use renewable sources, utilize carbon dioxide (CO_2) (Poliakoff et al., 2015), increase energy efficiency (Oncel, 2017) and

* Corresponding author.
E-mail addresses: camila@planlink.com.br (C.F.R. Machado), ofelia@eq.ufrj.br (O.Q.F. Araújo), jlm@eq.ufrj.br (J.L. de Medeiros), rmbalves@usp.br (R.M.B. Alves).

https://doi.org/10.1016/j.jclepro.2017.10.234
0959-6526/© 2017 Elsevier Ltd. All rights reserved.

reduce use of toxic, bio-accumulative and persistent substances (Anastas and Warner, 1998). These guidelines and principles are the leitmotiv for developing environment-oriented processes, with integration of chemical plants (sharing mass fluxes - products and reagents), substituting fossil derived carbon feedstocks by renewables and CO_2, structured as a chemical complex, herein named "environment-oriented integrated chemical plants", or Eco-Pole.

To emphasize the synergy of CO_2 utilization with the components of green and sustainable chemistry, a set of criteria to promote feasibility of different processes or reactions using CO_2 as feedstock to value-added chemicals have been defined, the principles of CO_2 Chemistry (Poliakoff et al., 2015). The main point is rather than treating CO_2 as waste, it can be regarded as a chemical feedstock for the synthesis of chemicals that do not rely on petrochemical sources. However, utilization of CO_2 as feedstock does not necessarily contribute to the mitigation of greenhouse effects, even though CO_2 stands as a green reactant in many cases (Sakakura et al., 2007). There are no easy solutions without involving major changes in the energy systems (Song, 2006) as the world energy demand is one order of magnitude higher than the amount of CO_2 fixed by chemical utilization of CO_2, which accounts for only 0.36% of global CO_2 emissions (Otto et al., 2015). Nevertheless, chemical conversion of CO_2 might contribute, through substitution of fossil feedstock, to reduce the volume of CO_2 produced.

Few processes utilize CO_2 in the chemical industry as successful commercial processes (Otto et al., 2015): synthesis of urea (50 Mtpa) (Aresta, 1999), salicylic acid (Song, 2006) and inorganic carbonates (20Mtpa) (Aresta, 1999). Nevertheless, chemical utilizations of CO_2 include many possible routes: production of carbonates, reduction of organic monomers and polycarbonates, and production of methanol and polyurethanes (Alves et al., 2014). Van-Dal and Bouallou (2013) studied the production of methanol from CO_2 hydrogenation, employing hydrogen from water electrolysis using carbon-free electricity, reporting reduction of CO_2 emissions. Wiesberg et al. (2016) studied carbon dioxide management by chemical conversion to methanol through comparison between hydrogenation and bi-reforming processes. The direct use of CO_2 and H_2 avoids many of the complications and variabilities dealt with in using syngas. As well, this feedstock is chemically similar to syngas and relies on the same technology as conventional methanol production (Matzen and Demirel, 2016). Omae (2006) lists a variety of products from CO_2 (formic acid, formic acid esters, formamides, methanol, dimethyl carbonate, alkylene carbonates, polycarbonate, among others). Otto et al. (2015) collected in the literature 123 reactions using CO_2 as raw material (23 to produce bulk chemicals and 100 to fine chemicals) and recognized the need of criteria for ranking the variety of alternatives with the greatest potential for CO_2 utilization: specific mass of CO_2 as a feedstock; CO_2 avoidance potential; relative added value; and independence from fossil reactants. Styrol and urea topped the rank followed by propylene carbonate, ethylene carbonate, diethyl carbonate and dimethyl carbonate. However, adding the scores of these four carbonates results in carbonates leading the rank. With similar result, Alper and Orhan (2017), reviewing current CO_2 utilization scenario, concluded that products resulting from carboxylation reactions are the obvious conversions (synthesis of carbonates, carbamates and carboxylates) in the short term.

Dimethyl carbonate (DMC) is among the most promising candidates, being a safe and nontoxic substitute for well-established methylating and carbonylating agents (e.g., phosgene), and having potential as an oxygen-containing fuel additive (Dai et al., 2009). Furthermore, DMC has great activity towards nucleophilic molecules (e.g., phenols), which makes it a valuable reactant for the production of other useful organics (Huang and Tan, 2014). Carbonilation of CO_2 by its reaction with ethylene oxide produces ethylene carbonate (EC) (Kawabe, 2010). Transesterification of EC with methanol is considered a promising route for large-scale commercial production of DMC, yielding as co-product high purity ethylene glycol (MEG).

Of relevance to the work, in Brazil, the sugarcane industry represents one of the most important economic activities producing sugar and ethanol for internal and external markets (Pina et al., 2015). In the internal market, ethanol has been used as a fuel for thirty years. More recently, attention is also being paid to bioethanol-derived chemicals as substitute of fossil feedstocks (Bastos, 2007). Despite sugar and alcohol being the main products in the bioethanol industry, the high purity CO_2 produced has been neglected as potential feedstock to chemical syntheses. It is a relevant motivation to this study that the production of bioethanol is associated with intense CO_2 emissions: 1 ton of processed sugarcane produces 50.6 L of ethanol and 39.7 kg of CO_2 from fermentation (Rodrigues, 2011). To increase sustainability, chemical utilization of CO_2 is demanded.

Several studies have been carried out regarding valorization and optimization of biorefineries. Although most of them concentrate efforts to improve economic performance (optimizing operating conditions) and add value to residues from sugarcane, just a few works deal with the integration of the bioethanol plant to the production of chemicals or chemical clusters. He and You (2015) simulated and optimized a bioethanol-to-ethylene process. Chinniyomphanich et al. (2016) evaluated the impacts of using a SAPO-based catalyst for catalytic dehydration of bio-ethanol to propylene. Matzen and Demirel (2016) investigated two renewable based alternative fuel: methanol and dimethyl-ether using wind-based electrolytic hydrogen and carbon dioxide captured from an ethanol fermentation process, reporting reduction of greenhouse gas emissions. Tsiropoulos et al. (2015) used life cycle assessment to compare fully bio-based high-density polyethylene and partially bio-based polyethylene terephthalate from sugarcane ethanol with the equivalent petrochemical production. Bioethanol-based polyethylene production resulted in 140% lower greenhouse gas emission than petroleum-based one, and save the non-renewable energy use by 65%. Moreover, Lundin (2011) investigate options for clusters of chemical process plants to decrease their energy and emission footprints. Sengupta and Pike (2013) applied process simulation to evaluate integration of bioprocesses into chemical production complexes. To the best of the authors knowledge, literature gaps on centering the chemical complex on CO_2 and bioethanol, both originated from a biorefinery, as main feedstock, neither focused on carbonates as main throughput of the complex.

Hence, based on the commercial scale production of carbonates (and polycarbonates) from CO_2, and methanol from CO_2 hydrogenation, this work presents an original integration of chemical plants exploring these CO_2 conversions, having DMC, EC and MEG as the main products. Also of noticeable novelty, the conceptual design results in an integrated environment-oriented chemical complex (Eco-Pole), aiming to promote sustainability of the sugarcane bioethanol industry using the high purity CO_2 from sugarcane fermentation and the produced bioethanol from a hypothetical nearby sugarcane biorefinery. Furthermore, since the Eco-Pole is located nearby the bioethanol biorefinery, distant from chemical suppliers, ethylene oxide is produced locally from bioethanol dehydration, restricting the use of exogenous feedstocks to propane, hydrogen peroxide and hydrogen. Other chemical plants are aggregated to the complex aiming to improve economic performance and sustainability, and plant capacities are designed to meet internal demand while producing surplus to exporting.

The Eco-Pole produces nine chemicals of major relevance to the chemical industry, namely methanol (MeOH), propylene, ethylene, ethylene oxide (EO), propylene oxide (PO), ethylene carbonate (EC),

propylene carbonate (PC), dimethyl carbonate (DMC) and ethylene glycol (EG). Many of the processes considered in the Eco-Pole herein evaluated are still in their early stage of technological development, but others are already industrially applied.

The performance of Eco-Pole is evaluated on technical, economic and environmental grounds, based on mass and energy balances obtained by process simulation. The environmental performance is herein evaluated based on sustainability metrics proposed by Araújo et al. (2015), where a Sustainability Degree is computed to ranking processes accordingly, supporting the decision-making procedure of configuring the Eco-Pole. Therefore, the analysis of sustainability metrics shows how a given process makes use of mass and energy inputs to produce a given product, considering environmental requirements, while maximizing its economic benefits (Ruiz-Mercado et al., 2013).

The inclusion of environmental aspects in feasibility analyses is of great relevance to improving sustainable engineering decisions (Matzen and Demirel, 2016). In this approach, resides the additional relevance of the present work, and its contribution, filling the gap of procedural sustainability analysis at early phases of engineering design, where decisions can effectively affect environmental performance at minimum cost. It is widely accepted that 80% of a product's overall environmental impact has been 'built in' by the end of the conceptual design phase (O'Hare et al., 2015).

2. Methods

The integrated chemical complex is evaluated through process engineering and simulation approach using ASPEN HYSYS (ASPENTECH INC) to calculate mass and energy balances. The selected processes are evaluated at industrial scale capacity, on technical, economic and environmental grounds. The thermodynamic and kinetic bases for process simulation are detailed in Appendices A and B of the Supplementary Material. Fig. 1 shows the design development steps for the Eco-Pole.

2.1. Processes and configuration of the eco-pole

The Eco-Pole integrates seven processes and nine main products, as depicted in Fig. 2. Availability of high purity CO_2 from a hypothetical nearby sugarcane refinery is assumed in the study. Based on the literature review, carbonates and methanol were identified as the CO_2 derived products with highest technology maturity (based on existent pilot or demonstration plants). These products demand feedstocks, mostly associated with difficulties for transportation either due to chemical instability (ethylene oxide) or logistics, as they are not available nearby bioethanol producing plants (normally located in the surroundings of sugarcane plantations, suppliers of bioethanol and CO_2). Consequently, these feedstocks were aggregated as products of the Eco-Pole.

The objective of integration is to explore the synergies between raw materials and products, in order to achieve maximum utilization of mass and energy requirements. The simulation of the integrated complex (Eco-Pole) allows evaluating its performance according to technical, economic and environmental criteria as well the benefits of the proposed CO_2 chemical sequestration. Furthermore, the study aims to identify weather exporting the production surplus is beneficial to the economic performance of the complex.

The integration maintains all premises and operating conditions of each unit unchanged. It is worth noticing that production capacity of each unit was defined to meet both internal and external demands (exported from the Eco-Pole to the market), aiming for increased revenues and larger capacities, which results in economy of scale.

The bioethanol availability was the main capacity determining factor. From ANP - Brazilian Regulatory Agency of Oil, Gas and Biofuels (2017), there are several bioethanol plants with different capacities in Brazil, from 149.8 km^3/year (Brazilian Northeastern region) to 700 km^3/year (Brazilian Central Region), with average capacity of 282.3 km^3/year. The larger the bioethanol plant, the higher the CO_2 supply, and larger chemical plants in the Eco-Pole would be possible, benefitting from economy of scale. As design premise, the Eco-Pole was sized to receive the CO_2 emitted by a 479 km^3/year, taken as the arithmetic mean of the average capacity

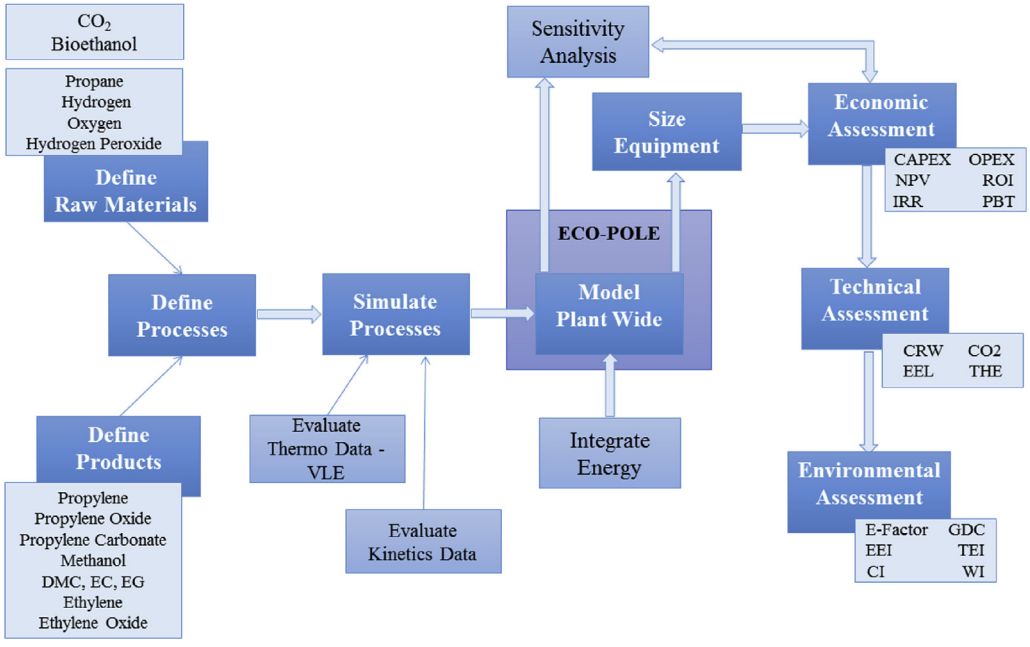


Fig. 1. Design development steps of the Eco-Pole.

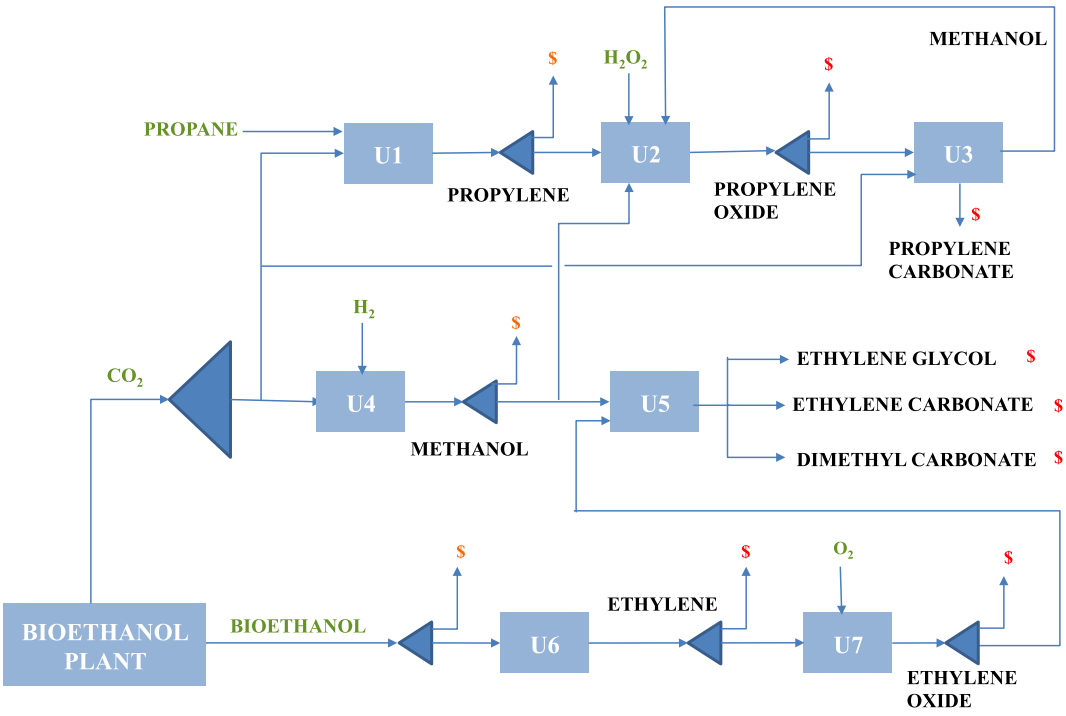


Fig. 2. Proposed Eco-Pole centered in CO_2: U1 - propylene production unit; U2 - PO production unit, U3 - PC production unit; U4 - methanol production unit; U5 - DMC, EC and EG production unit; U6 - ethylene production unit, and U7 - EO production unit. $ stands to product sale.

and the largest capacity of bioethanol plant in Brazil. Furthermore, considering that 1 t sugarcane ferments to yield 39.7 kg CO_2 and 40.48 kg bioethanol (with density of 800 kg/m^3), 46,981 kg/h of CO_2 were set as feedstock to the Eco-Pole. Based on this, the annual production of the main products from the Eco-Pole is shown in Table 1, considering 8000h/year of operation,.

Additionally, CO_2 needs to be compressed to achieve the reactions operating conditions. So, the pressure for the CO_2 feed stream is set at 5 bar for simulation purposes.

2.1.1. Process description

Propylene (C_3H_6) is produced by dehydrogenation of propane (C_3H_8) in the presence of CO_2. In this reaction, CO_2 acts as an oxidant to combine the dehydrogenation of C_3H_8 with a reverse water gas shift, and hence, the equilibrium of the dehydrogenation of C_3H_8 can be shifted to the product side (Du et al., 2015). The presence of CO_2 increases the propylene yield and reduces catalyst deactivation (Du et al., 2015; Takahara et al., 1998).

The dehydrogenation of propane to propylene using CO_2 occurs at 550 °C, with propane conversion of 53.3%. Under these conditions, selectivity is 79% for propylene, 20.5% for CH_4, and 0.5% for C_2H_4. Based on Wu et al. (2013) the reactor is simulated as a conversion reactor model. The reactor output stream follows to the purification step, which is comprised by three stages for water removal and separation columns. First, propane and propylene are absorbed by n-octane and non-reacted CO_2 is removed and recycled to the hydrogenation reactor. Propane and propylene are then separated by distillation in order to specify propylene product as 99.8% (weight). Propane is recycled to the reaction step. The unit is simulated to supply the demand of propylene for the propylene oxide unit in the Eco-Pole and also for external demand, i.e., surplus is commercialized to the market.

About 50% of the total production of propylene is consumed by the propylene oxide production unit, in which, propylene oxide is produced by epoxidation reaction, using hydrogen peroxide (H_2O_2).

In this work, the epoxidation of propylene with H_2O_2 occurs with excess of methanol and in the presence of TS-1/SiO_2 catalyst in an isothermic tubular reactor. The increase in concentration of H_2O_2 reduces the selectivity towards propylene oxide (PO), while increasing methanol concentration improves the selectivity. Increasing pressure and temperature promotes enhanced PO selectivity (Wu et al., 2013). The reactor is simulated at 40 °C and 4 bar, using a kinetic model as described in Appendix B (Supplementary Material). After the reactor, a separation step comprising of three distillation columns is used to specify propylene oxide product as 96% (weight) and remove non-reacted H_2O_2 and methanol, which are recycled to the reactor. Approximately 50% of the total propylene oxide production is dedicated to internal feedstock request for the carbonate propylene unit.

Propylene carbonate (PC) is synthesized by the reaction between propylene oxide (PO) and CO_2 (Li et al., 2012). Thus, the unit consumes CO_2 directly and indirectly through the use of PO from the Propylene Oxide Unit. The reaction is simulated using a kinetic model at 320 °C and 11.5 bar. After the reaction step, pure

Table 1
Annual production of the eco-pole units[a].

Products	Production (kt/year)	Fraction of the annual production to external demand (%)
Methanol	114.02	20.50
DMC	28.42	100
Ethylene	300.00	67.00
Propylene	56.32	53.38
Ethylene Oxide	133.28	84.57
Propylene Oxide	37.02	49.89
Ethylene Carbonate	14.71	100
Propylene Carbonate	29.98	100
Ethylene Glycol	18.84	100

[a] 8000 h of operation per year were considered.

propylene carbonate is separated from non-reacted ethylene oxide, which is recycled to the reactor. All propylene carbonate produced is commercialized to the market.

In the unit 4 (U4), methanol is synthesized by CO_2 hydrogenation. The synthesis of methanol by hydrogenation of CO_2 is divided into three reversible and independent reactions. The global reaction is favored by low temperatures and high pressures, which increase methanol selectivity and yield. Despite the fact that CO_2 conversion increases with the increase in temperature, yield and selectivity are reduced (Graaf et al., 1988). So, the reaction takes place at high pressure with low conversion of approximately 20%, recycling the non-reacted gases to increase the process yield (Mota et al., 2014). Fresh hydrogen and CO_2 are supplied to the unit at 20 bar and 5 bar, respectively. Before entering the reactor, CO_2 and hydrogen streams are heated to 220 °C at 39.5 bar. A ratio H_2/CO_2 equal to 3 is assumed in the reactor inlet, which operates adiabatically.

The reactor outlet stream is condensed to 10 °C, by using a propane refrigeration cycle. After, the condensate is separated from the gas phase, constituted by non-reacted CO_2 and H_2, which are recycled to the reactor. The liquid phase, rich in methanol, is then purified to achieve the desired specification (99.1% weight). The unit is simulated to supply methanol to the DMC and PO units as well to the market.

About 20% of the produced methanol reacts with fresh CO_2 and ethylene oxide (EO) to produce dimethyl carbonate (DMC) and ethylene carbonate (EC). Ethylene glycol (EG) is obtained is by-product. The process involves the formation of EC from CO_2 and EO reaction followed by conversion of the intermediary EC into DMC and EG. The first reaction occurs in a tubular reactor at 39.5 bar and 100 °C to produce EC with conversion and selectivity of 100%, approximately. The second reaction occurs in a tubular reactor at 71 °C and 100 bar and excess of methanol. Kinetic models are assumed for simulation. In both cases, the non-reacted compounds are recycled to the respective reactors, after separation. The separation step is composed by three distillation columns and one extractive column to specify the products for commercialization. The columns operate at sub-atmospheric pressures.

In the context of the proposed Eco-Pole, operating in synergy with the bioethanol plant, the production of green ethylene by bioethanol dehydrogenation is considered. Recently, green-ethylene plants in Brazil and India represent about 0.3% of the worldwide ethylene capacity (IEA-ETSAP and IRENA, 2013).

The bioethanol stream is heated in a furnace to achieve the reactor condition, 375 °C and 7.5 bar. The dehydrogenation reaction occurs in the presence of an aluminum based catalyst in a multi-tubular reactor. The reaction network for ethylene synthesis comprises consecutive parallel reactions with diethyl ether (DEE, $(C_2H_5)_2$) as an intermediary product. The main products of ethanol (C_2H_5OH) dehydrogenation are ethylene, DEE, acetaldehyde and butenes.

The reaction is simulated by a conversion reactor model, based on the conversion of ethanol and selectivity of products, from which the conversion of each reaction is estimated.

After the reaction step, the water formed during reaction is condensed and removed. Two distillation columns are used to separate ethylene from the other co-products. Ethylene is specified as 99.8% (weight). Hydrous ethanol is considered to increase the unit revenue.

Ethylene oxide production is achieved by direct catalytic oxidation of ethylene with oxygen (O_2). The EO unit is composed by reaction, absorption and purification steps. The reactions take place in a tubular reactor at 220 °C and 20 bar. Under these conditions, conversion of ethylene is around 10%–12%, with ethylene oxide selectivity between 78% and 82%. The formation of CO_2 occurs in parallel with the formation of ethylene oxide. The reactions are simulated as a kinetic model. Ethylene oxide from the reactor effluent stream, after absorption with water, is purified at 99.5% (weight) by two distillation columns. The non-absorbed co-products are recycled to the reactor.

Unit U7 was designed according to a commercial ethylene oxide unit and the separation step was designed to achieve the commercial product specification.

The proposed process flowsheets simulated in ASPEN HYSYS and the mass balances for each unit and integrated complex are respectively presented in Appendices C and D in the Supplementary Material, available on line.

3. Results and discussion

3.1. Technical performance

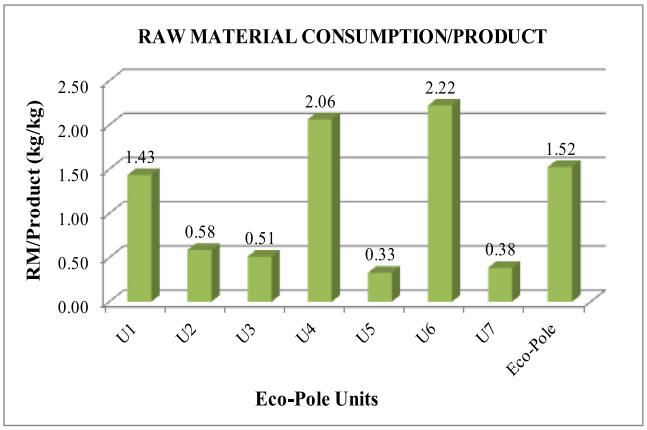
Consumption of raw materials, electric energy and thermal energy were used as CO_2 emissions indexes in order to compare the efficiency of each process with the performance of the Eco-Pole. It is understood that consumed energy has two sources: electric, from compressors and pumps, and thermal, from the consumption of vapor. CO_2 emission was computed as the amount of CO_2 released for electric energy and vapor generation. In the conversion of these indexes, the following correlations were used: (1) for each 1 kJ of thermal energy consumed, 5.537×10^{-8} t CO_2 is generated; (2) for each 1 kJ of electric energy consumed, 8.009×10^{-8} t CO_2 is generated (Dickinson et al., 2012). Evaluation of the technical indexes regarding the production of each unit is presented in Fig. 3.

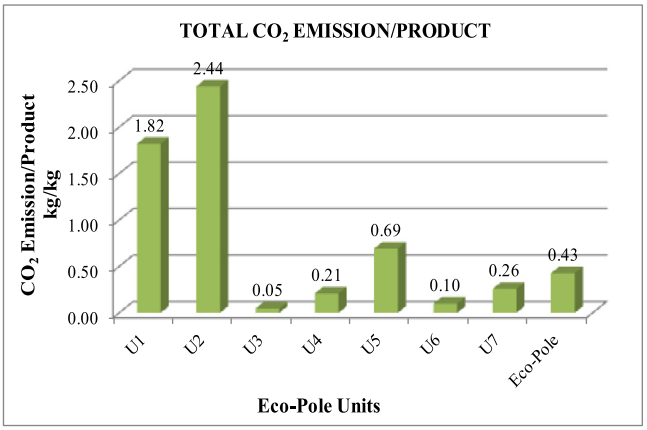
Concerning the index consumption of raw materials per product produced, CO_2 and exogenous feedstocks are the raw materials considered as calculation reference, i.e., CO_2 is the raw material for the units U1,U3, U4 and U5; H_2O_2, bioethanol and oxygen are the raw materials for the units U2, U6 and U7, respectively.

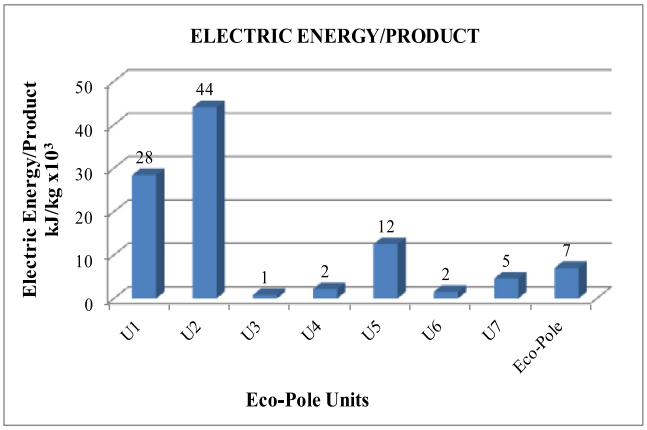
The consumption of raw materials per product is higher for unit U6, Ethylene Unit, followed by units U4 and U1, Methanol and Propylene Units, respectively, which represents low conversion of the raw material. The index electric energy/product shows higher consumption in the units U1 and U2, Propylene and Propylene oxide units, respectively. The high consumption is due mainly to the columns operating pressure and compression in the U1. The thermal energy per product shows high consumption in the units U1 and U4.

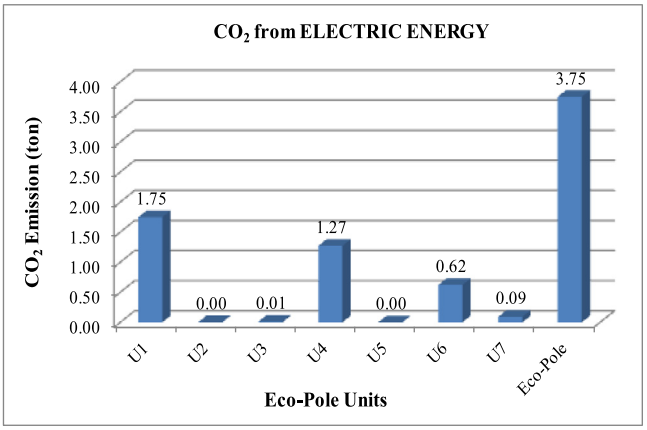
The consumption of electric and thermal energy was converted in CO_2 emission to quantify the performance of the Eco-Pole in sequestering CO_2. Clearly, the lower the consumption of thermal and electric energy, the lower the CO_2 generation from consumption of utilities and, consequently, the better the performance of the chemical complex. In Fig. 4, units U1 and U2 present higher specific CO_2 emissions associated with the total energy consumption, which penalize the integrated plant with regard to the reduction of CO_2 emissions. Units U1and U4 are responsible for the highest CO_2 emission from electric energy. Concerning the rate of CO_2 emissions associated with use of thermal energy, U2 and U1 present the highest emission: 2.44 and 1.57 t CO_2 per ton of product, respectively. Units U3, U4 and U7 show favorable performance with respect to the general objective of the Eco-Pole, i.e., to reduce CO_2 emissions. Overall, CO_2 emissions per ton of product in the Eco-Pole are low (Fig. 4).

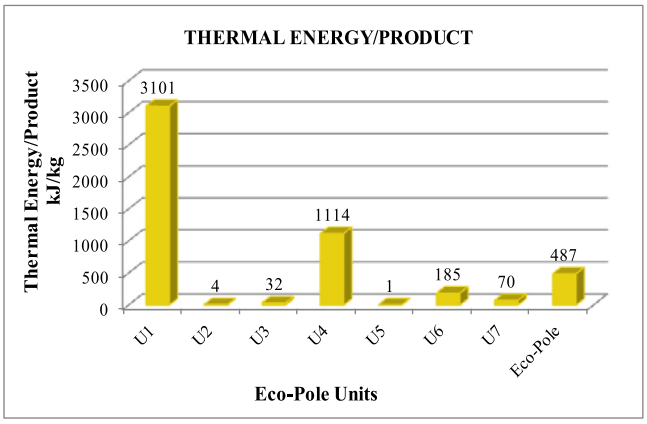
The CO_2 emission is related to electric and thermal energy. Additionally, the CO_2 purchased from the sugarcane biorefinery is considered as an environmental passive to be remediated through conversion to chemicals in the Eco-Pole. Hence, unconverted CO_2 is a residual passive owned by the Eco-Pole, which holds the onus of the resulting emission.











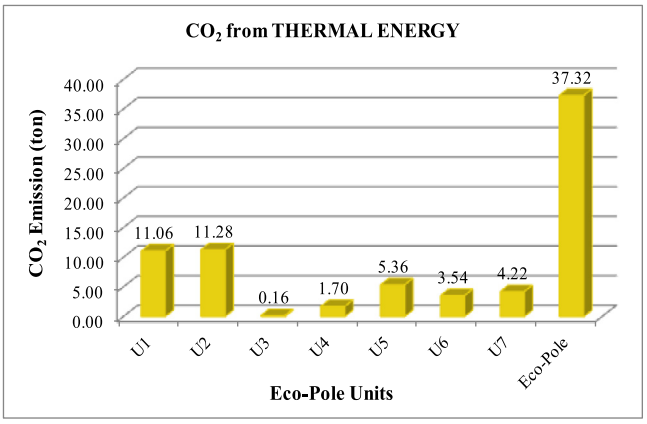


Fig. 3. Echnical Indexes of Eco-Pole units and its global performance.

Fig. 4. Analysis of CO_2 emissions associated with energy consumption in the Eco-Pole.

3.2. Economic performance

Capital cost estimate of the Eco-Pole, based on the methodology presented by Turton et al. (2012), is used to compare alternative technologies. To consider the effect of time on equipment costs, the Chemical Engineering Plant Cost Index (CEPCI) of 2014, cited in the Chemical Engineering (2015) magazine, is used. Since CAPEX (Capital Expenditure) estimation from Turton et al. (2012) reflects the United States industrial scenario, values are corrected to represent the Brazilian context using a "nationalization factor" (multiplication factor) of 1.4. Table 2 presents a cost summary of the utilities used in the evaluation. Natural gas-fired furnaces are considered.

The values of price for feedstocks and products are presented in Table 3. In the survey undertaken to obtain these values, recent references were not available in the open literature for a few products, and constitutes a discrepancy with respect to CAPEX, which is updated to 2015 by the CEPCI. However, with the absence of more recent data, this critical point, although recognized, is admitted in the economic evaluation. Nevertheless, due to comparative purposes, this aspect is not anticipated to impact conclusions.

The price of DMC is estimated in comparison to the price of methanol. As well, the cost of H_2 was estimated in comparison to the price of natural gas. The market value of 1-butene/ethyl ether was ascertained based on the premise that it was equal to the value of 1-butene. Similarly, the price of propylene carbonate was considered equal to the price of ethylene carbonate.

Table 2
Cost of utilities.

Utilities	Cost
Natural Gas	7.78 US$/GJ
Saturated LP vapor	0.0492 US$/kg
Saturated HP vapor	0.0514 US$/kg
Electric Energy	46.56 US$/GJ [(1)]
Cooling water (USD/t)	0.03 US$/t [(2)]

[(1)]Firjan, 2015; [(2)] Ferreira et al., 2013.

Table 3
Price of products and feedstocks.

Product/Raw material	Value (US$/kg)	Reference
Methanol	0.466	ALICEWEB (2015) [a], Methanex Corporaton (2017)
CO_2	0.003	Parsons Brinckerhoff (2011) [b]
Bioethanol	0.696	UDOP (2015)
Bioethanol 70%	0.61	UDOP (2015)
H_2	0.87	Wiesberg et al. (2016) [c]
Ethylene	1.30	Boehe (2012) [d], Lippe (2016)
1-Butene/Ethyl ether	0.748	ICIS (2008)
Ethylene glycol	1.562	Ong (2014) [e], ICIS (2014a,b,c)
O_2	0.21	NasaFacts (2006)
Ethylene oxide	1.683	Tecnon OrbiChem (2013) [f], ICIS (2014a,b,c)
Propylene oxide	2.22	ICIS (2011) [g], ICIS (2014a,b,c)
H_2O_2	0.77	ICIS (2008), Alibaba (2017a,b,c) [h]
Propane	1.01	EIA (2015)
	0.207	Argus (2014)
Propylene	1.50	ICIS (2008), ICIS (2014a,b,c) [i]
DMC	1.165	–
Ethylene carbonate	1.70	ICIS (2008), Alibaba (2017a,b,c)
Propylene carbonate	1.70	Alibaba (2017a,b,c) [j]

[a] ALICEWEB is the system of evaluation of Brazilian foreign trade. An average value, for the year 2014 was used.

[b] The price for pipelined CO_2 has historically been in the range of US$9-US$26/t, which incorporates the cost of the pipeline infrastructure (capital and operational costs). According to Parsons Brinckerhoff and Global CCS Institute (2011), the price of bulk CO_2 is set through private negotiations between parties and not available for public scrutiny. Since the Eco-Pole is responsible for transporting/compressing CO_2, the main cost component of CO_2 supply, the bioethanol plant is assumed to set CO_2 price as 1/30 of the lower limit of pipelined CO_2 (US$9/t).

[c] Hydrogen from biomass is assumed, with price ranging from 866 to 1200 $/t.

[d] Ethylene price of $800/t, for oil price of $60/barrel. According to Boehe (2012), whenever oil price increases $10, ethylene price rises $120/t. The price $1.3/kg corresponds to oil price of $64.2/barrel.

[e] Ethylene glycol prices are likely to remain volatile. Demand from EG has eased off slightly as the PET resin season winds down Tecnon OrbiChem (2013). The Eco-Pole analysis adopts the price of 1.562 US$/t. It is worth noting that such volatility impacts the economic performance of the Eco-Pole.

[f] Price volatility is high. The value adopted (1.683 US$/t) occurs for some months in 2008, 2011, 2012 and 2013, in price historical presented by Tecnon Orbichem (2013).

[g] Volatility of propylene oxide occurs due to consumption being largely tied in with the making of polyether polyols, whose growth in demand is largely dependent on use in polyurethane (PU) foam.

[h] Price from ICIS (2006) is in the range of prices found in the online trading platform, Alibaba.com. The former was adopted.

[i] Price from ICIS (2008) is in the range of prices in March 2014, varying from US$1405.45/t (R Grade) to US$ 1554.26 (P Grade).

[j] Upper value in the range of prices found in the online trading platform, Alibaba.com. Same value adopted for ethylene carbonate was used.

Table 4 presents the cost of raw materials (CRM) and revenues with the sale of products, in US$/year. In the economic estimate, produced saturated steam was considered as a source of revenue.

3.2.1. CAPEX, OPEX and cash flows

A realistic evaluation of profitability requires data on revenue, working capital, depreciation, taxes, discount rates, etc., as well as capital and operational costs. Discounted cash flows are calculated for 20 years of project lifetime, for each plant. The construction period is considered to be 2 years. Total fixed capital investment is represented by the *grass roots cost* (GRC), considered to be distributed over the construction period (60% in year 1 and 40% in year 2). Depreciation is calculated by the MACRS (*Modified Accelerated Cost Recovery System*) method from the third year after the end of investment and the beginning of plant operations (Turton et al., 2012). Land costs are not considered. For net profit and cash flow, a total tax rate of 45% is used. In the discounted cash flow, the risk rate is 10%. Knowing that chemical process plants operate beyond 20 years, perpetuation of the investment is used in the accumulated cash flow calculation, discounting the NPV (Net Present Value) for the 20th year of operation, which is equivalent to correcting the NPV by the depreciation rate of 10%.

Table 4
Cost of raw materials (RM) and revenues (products, P) in the integration of the Eco-Pole Units.

	Raw Material (RM)/Product (P)	Cost/Revenue (US$/year)
Propane	RM	72,412,960
CO_2	RM	1,127,544
H_2O_2	RM	16,650,480
H_2	RM	28,271,520
Bioethanol	RM	520,329,600
Saturated Steam (HP)	RM	591,581
O_2	RM	10,746,960
Saturated Steam (LP)	RM	1,133,962
Total cost of raw materials:		**651.264.607**
Ethylene oxide	P	147,565,440
Ethylene	P	251,472,000
Ethanol 70%	P	87,644,800
1-Butene/Diethyl ether	P	36,819,552
Methanol	P	55,882,720
DMC	P	74,485,440
Propylene oxide	P	31,416,000
Propylene carbonate	P	50,972,800
Saturated LP Steam	P	9,639,264
Saturated HP Steam	P	20,217,059
Ethylene carbonate	P	55,284,000
Propylene	P	31,692,000
Ethylene glycol	P	66,328,768
Total Revenue:		**919,419,843**

The economic evaluation is undertaken for each unit individually, maintaining the conditions presented in the integrated plant, except product flows (Fig. 5). Based on these results, it can be observed that the propylene oxide production unit presents the best performance and the ethylene production unit has the worst economic performance. Besides, two scenarios is evaluated concerning EG commercialization (Fig. 5 (f) and (g)). The Brazilian EG market is currently saturated and absorbing the EG production could be a challenge. However, in a near future, this situation tends to change and the market should become favorable to EG commercialization. Due to the natural gas market expansion, it is expected an increasing demand for EG. In this case, the commercialization and revenue should be considered, as herein adopted.

3.2.2. Integrated complex - The Eco-Pole

In the integration of the units, part of the products from a given unit is directed as raw material to another unit, to reduce production costs and increase revenues with higher value-added products. Fig. 6 shows CAPEX as the percentage contribution of each item of equipment in the integrated plant, in which the greatest portion is due to the columns; i.e., the separation stages. The total cost of utilities is dominated by the high consumption of electricity in

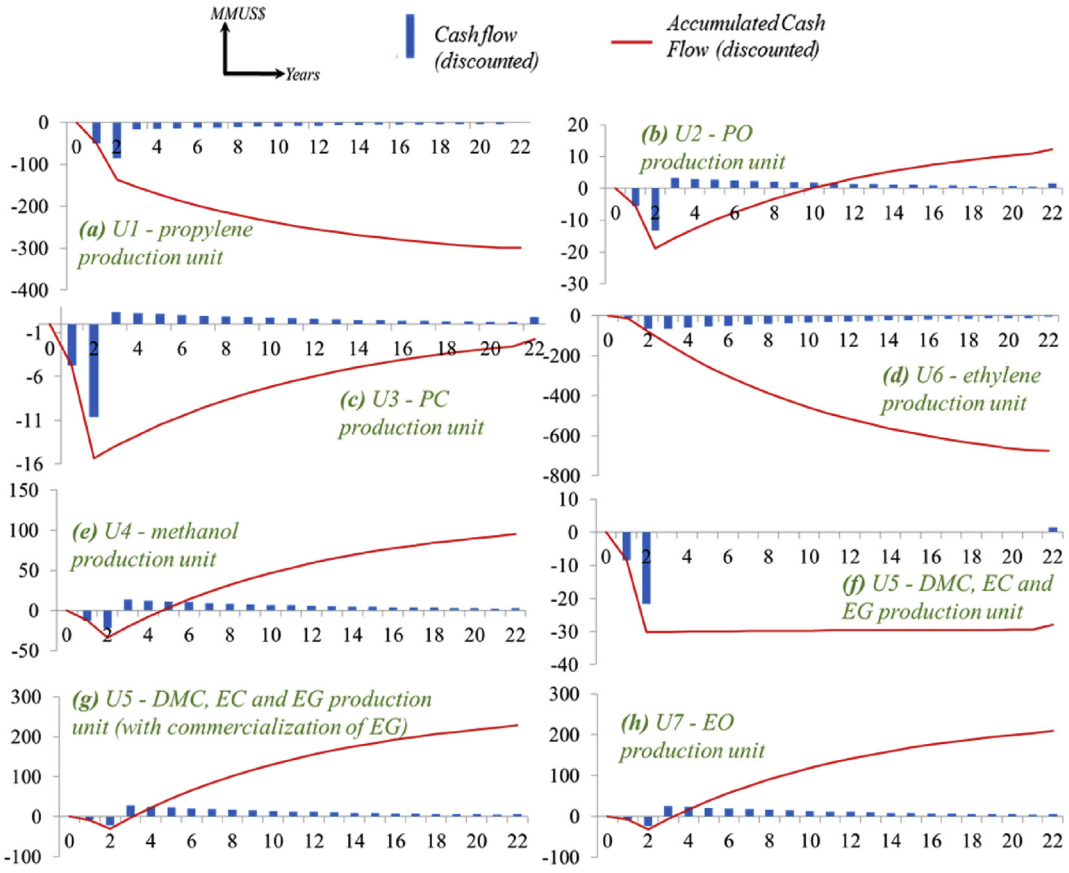

MMUS$
Years
Cash flow (discounted)
Accumulated Cash Flow (discounted)
(a) U1 - propylene production unit
(b) U2 - PO production unit
(c) U3 - PC production unit
(d) U6 - ethylene production unit
(e) U4 - methanol production unit
(f) U5 - DMC, EC and EG production unit
(g) U5 - DMC, EC and EG production unit (with commercialization of EG)
(h) U7 - EO production unit

Fig. 5. Cash flows: (a) U1 - propylene production unit, (b) U2 - PO production unit, (c) U3 - PC production unit, (d) U6 - ethylene production unit, (e) U4 - methanol production unit, (f) U5 - DMC, EC and EG production unit, (g) U5 - DMC, EC and EG production unit (with commercialization of EG), (h) U7 - EO production unit.

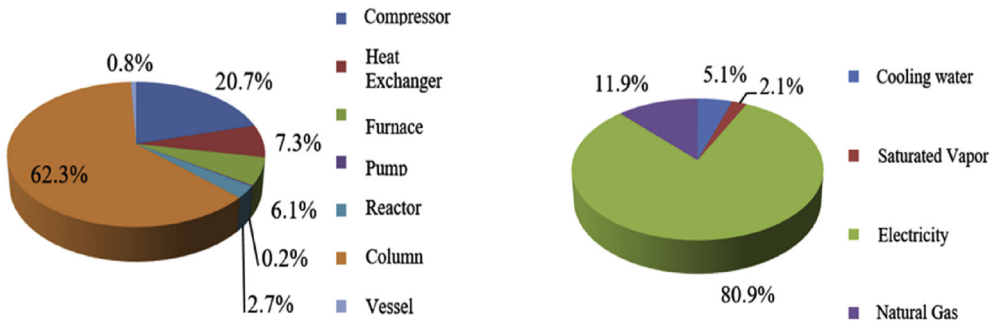


Fig. 6. Contribution of each item of equipment to the CAPEX and contribution of each item of equipment to the total cost of units in the integrated plant.

compressors, i.e., moderate operating conditions with milder pressures must be prioritized. A trade off exists as this increases the cost of larger catalytic reactors while reducing the cost with compression of raw materials. Table 5 presents the main results of the economic analysis through the methodology proposed by Turton et al. (2012).

Plant integration under the adopted conditions (Base Case) does not present a positive NPV (Net Present Value) (Fig. 7).

3.3. Environmental performance

For evaluation of environmental performance, Sustainability Degree (SD) index is used, derived from a multi-criteria analysis (MCA) suggested by Araújo et al. (2015). MCA uses quantitative metrics which measure environmental and economic performances and *ad hoc* principles compiled from CO_2 Chemistry (Poliakoff et al., 2015) and green engineering (Anastas and Zimmerman, 2003).

The quantitative environmental metrics employed are E-factor (material efficiency), Electric Energy Intensity (EEI), Thermal Energy Intensity (TEI), Carbon Intensity (CI) and Water Intensity (WI) (Araújo et al., 2015). Table 6 displays the Green Degree Criticality Factor, based on *ad hoc* criteria (Araújo et al., 2015), where U1 (propylene production) and U6 (ethylene production) are the components of the Eco-Pole that most contribute to degrading environmental performance.

Table 7 contains results of the quantitative metrics of environmental performance. E-Factor presents the worst performance for

Table 5
Results of the economic analysis of the integrated plant (Base case).

Item	US$/year
CAPEX	266,700,000
Revenue	919,419,843
OPEX	893,361,623
Cost of Raw Materials	651,264,606
Cost of Utilities	35,600,000
Cost of Labor	185,564

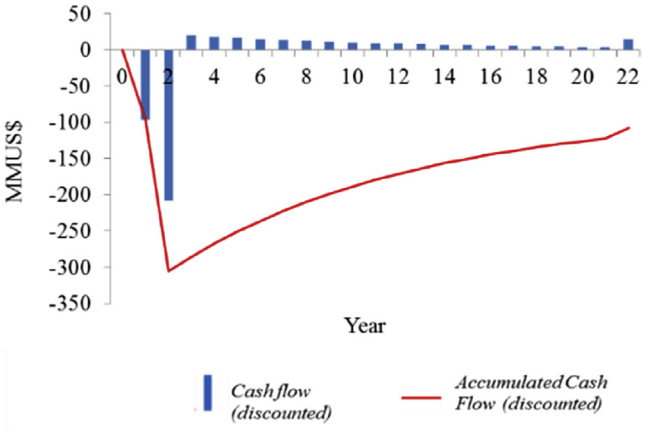


Fig. 7. Cash flow from the integrated plant (Base case).

Table 6
Results for green degree criticality factors[a].

	U1	U2	U3	U4	U5	U6	U7	CSIC
Average	2.00	1.29	1.14	1.43	1.43	2.00	1.29	1.71

[a] Araújo et al. (2015).

Table 7
Environmental and economic metrics[a].

	Environmental metrics					Economic metrics
	E-Factor	EEI	TEI	CI	WI	VPL (MMUS$)
Eco-Pole	2.12	0.022	0.32	−0.44	0.72	−108.3

[a] Araújo et al. (2015).

the Ethylene Production Unit, U6.

Sustainability Degree (SD) for each unit of the Eco-Pole is presented in Table 8.

The economic metrics (ROI and NPV) dominate the Severity Index for units U1 (propylene production), U3 (PC production) and U4 (methanol production). Clearly, the sustainability of these units would only be possible through optimization of the economic performance, or as a result of a more comfortable margin between revenue and operational costs. U7 (EO production), on the other hand, has its sustainability threatened by the E-factor metric: material efficiency (which could only be improved with technological advances in the process, with the development of more selective catalysts and greater conversion rates by reactor pass). With regard to U2 (PO production), the Severity Index is dominated by the intensity of thermal energy, carbon and water, requiring significant technological advances on these three fronts.

Table 8
Severity matrix and degree of sustainability of the Eco-Pole units[a].

	GDCI	E-Factor	EEI	TEI	CI	WI	VPL	ROI	SD
U1	2.00	9.00	1.00	3.00	1.00	3.00	9.00	9.00	1.43
U2	1.29	3.00	1.00	9.00	9.00	9.00	3.00	9.00	2.10
U3	1.14	1.00	1.00	1.00	1.00	1.00	9.00	9.00	7.95
U4	1.43	3.00	1.00	1.00	1.00	1.00	3.00	3.00	5.38
U5	1.43	1.00	1.00	3.00	1.00	1.00	1.00	1.00	7.78
U6	2.00	9.00	1.00	1.00	1.00	1.00	1.00	1.00	3.33
U7	1.29	3.00	1.00	1.00	1.00	1.00	1.00	1.00	8.64
Eco-Pole	1.71	3.00	1.00	1.00	1.00	1.00	9.00	9.00	2.33

[a] Araújo et al., 2015.

Evaluation of the Eco-Pole reveals a negative performance regarding economic metrics, which impact the degree of sustainability. The E-Factor shows also a negative performance due to the correlation between consumption of raw material and the Eco-Pole capacity. Regarding environmental metrics, it proved to be positive due to the synergy between the productive interactions of the units.

3.4. Sensitivity analysis

Knowing that the Ethylene Oxide Unit (U7) presents the best performance among the Eco-Pole units, and that the Propylene Unit (U1) has the worst economic performance, scaling up and down their production is evaluated within a sensitivity analysis. In the analysis, production scale of both units is varied from +20% (Case 1) to −20% (Case 2). Case 1 is economically unfeasible with negative NPV after 20 years of operation (Table 9). However, Case 2 presents feasibility with a NPV of US$169.44 MM in 20 years of operation and IRR (Internal Rate of Return) of 17.87%. Results are presented in Fig. 8 and Table 9.

In Case 2, CAPEX, OPEX, cost of raw materials and cost of utilities are reduced. Revenue undergoes a slight increase, which in turn increases cash flow and finally NPV.

4. Conclusion

CO_2 conversion is of interest due to the economic and environmental gains that can potentially be made through its development. Evaluation of CO_2 emissions objectively demonstrates that the performance indexes of the Eco-Pole outperforms individual units as a consequence of the synergy between the production plants of the integrated complex. Based on the economic performances, U2, U4, U5 (with EG commercialization) and U7 are economically feasible. Sensitivity analysis of the economic performance to the destination of the available CO_2 input among the producing units show that the Eco-Pole becomes economically feasible through downscaling in the U1 and upscaling in the U7. Considering these results, it is possible also to conclude that propylene and ethylene units should produce just to meet internal demand of the Eco-Pole, and for logistic issue, exporting ethylene and propylene would be not feasible. However, both units are included due to unavailability of infrastructure to transport these products to the industrial installation located close to sugarcane

Table 9
Result of the economic correlations of the sensitivity analysis.

	Case 1	Base Case	Case 2
CAPEX (MMUS$/year)	275	267	227
Revenue (MMUS$/year)	1023	930	941
Cost of raw materials (MMUS$/year)	784	651	617
Cost of utilities (MMUS$/year)	39	36	33
OPEX (MMUS$/year)	1062	893	840

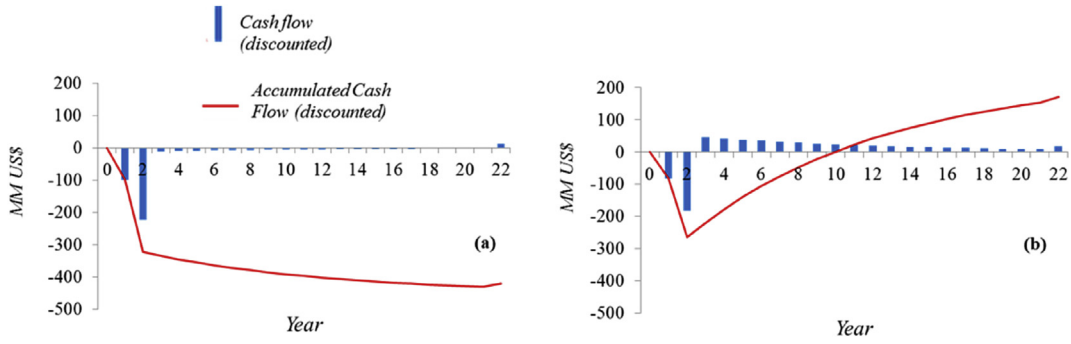


Fig. 8. Cash Flow sensitivity: (a) Case 1, (b) Case 2.

plantation. A more rigorous analysis should be conducted to determine the best economic and environmental configuration for Eco-Pole. However, an optimization procedure is out of scope of this work.

Although optimal performance remains to be sought, this work suggests that an Eco-Pole centered on converting high purity CO_2 from a sugarcane biorefinery can be economically feasible. With respect to the environmental performance, the Eco-Pole benefits from the synergies among the integrated units, which reduce environmental impacts. An unexplored approach is recovering pure CO_2 emitted from the ethylene oxide, which could increase the Eco-Pole yields.

Finally, the sustainability analysis permits identifying technological bottlenecks, which guides future research developments.

Acknowledgements

O.Q.F. Araujo and J.L. Medeiros gratefully acknowledge financial support from CNPq, Brazil, through Grant Proc. 310630/2013-4, 405851/2013-8 and 309640/2016-4. R.M.B Alves gratefully acknowledges support from Shell and FAPESP through the “Research Centre for Gas Innovation - RCGI” (FAPESP Proc. 2014/50279–4), hosted by the University of Sao Paulo, and the strategic importance of the support given by ANP (Brazil's National Oil, Natural Gas and Biofuels Agency) through the R&D levy regulation.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jclepro.2017.10.234.

Abbreviations

CAPEX	Capital Expenditure
CI	Carbon Intensity
CRM	Cost of Raw Material
DEE	Diethyl Ether
DMC	Dimethyl Carbonate
EC	Ethylene Carbonate
EEI	Electric Energy Intensity
EG	Ethylene Glycol
EO	Ethylene Oxide
GDCF	Green Degree Criticality Factor
IRR	Internal Rate of Return
MCA	Multi-Criteria Analysis
MeOH	Methanol
NPV	Net Present Value
OPEX	Operational Expenditure
P	Product
PC	Propylene Carbonate
PO	Propylene Oxide
ROI	Return of Investment
RM	Raw Material
SD	Sustainability Degree
TEI	Thermal Energy Intensity
U1	Propylene Unit
U2	Propylene Oxide Unit
U3	Propylene Carbonate Unit
U4	Methanol Unit
U5	DMC, EC and EG Unit
U6	Ethylene Unit
U7	Ethylene oxide Unit
WI	Water Intensity

References

Alibaba. https://wholesaler.alibaba.com/product-detail/Manufacturer-Direct-Supply-Industrial-Grade-Hydrogen_60542125888.html?s=p. (accessed: June/2017).
Alibaba. https://www.alibaba.com/product-detail/New-hot-selling-Propylene-Carbonate_60510340750.html?spm=a2700.7724838.0.0.MGjtQ7&s=p. (accessed: June/2017).
Alibaba. https://www.alibaba.com/showroom/ethylene-carbonate-price.html. (accessed: June/2017).
ALICEWEB. Sistema de Análise das Informações de Comércio Exterior. http://aliceweb.mdic.gov.br (accessed: January/2015).
Alper, E., Orhan, O.Y., 2017. CO_2 utilization: developments in conversion processes. Petroleum 3, 109–126.
Alves, R.M.B., Fontes, F.M., Medeiros, J.L., Araújo, O.Q.F., 2014. Trends in CO_2 capture, transport and utilization. In: 2014 AIChE Annual Meeting.
Anastas, P.T., Eghbali, N., 2010. Green chemistry: principles and practice. Chem. Soc. Rev. 39, 301–312.
Anastas, P.T., Kirchhoff, M.M., 2002. Origins, current status, and future challenges of green chemistry. Acc. Chem. Res. 35, 686–694.
Anastas, P.T., Warner, J.C., 1998. Green Chemistry: Theory and Practice. Oxford University Press, New York.
Anastas, P.T., Zimmerman, J.B., 2003. Design through the 12 principles green engineering. Environ. Sci. Technol. 37 (5), 95A–101A.
ANP -Brazilian Regulatory Agency of Oil, Gas and Biofuels (2017). Available at: http://www.anp.gov.br/wwwanp/images/publicacoes/boletins-anp/Boletim_do_Etanol/Boletim_do_Etanol_No09_FEVEREIRO_2017.pdf.
Araújo, O.Q.F., Medeiros, J.L., Yokoyama, L., Morgado, C.R.V., 2015. Metrics for sustainability analysis of post-combustion abatement of CO_2 emissions: microalgae mediated routes and CCS (carbon capture and storage). Energy 92 (P3), 556–568.
Aresta, M., 1999. Perspectives in the use of carbon dioxide. Quím. Nova 22 (2), 269–272.
Argus, 2014. Key Prices. http://www.argusmedia.com/methodology-and-reference/key-prices. (Accessed December 2014).
Bastos, V.D., 2007. Ethanol, Alcoolquímica e Biorrefinarias, vol. 25. BNDES Setorial, pp. 5–38. https://web.bndes.gov.br/bib/jspui/handle/1408/1305. (Accessed March 2015).
Boehe, D.M., 2012. Braskem: the Construction of a Global Scale Petrochemical Company. INSPER, Instituto de Ensino e Pesquisa. AE-P0020, (in Portuguese). https://www.insper.edu.br/wp-content/uploads/2013/10/Caso_Braskem_port.pdf.
Brinckerhoff, Parsons, 2011. Accelerating the Uptake of CCS: Industrial Use of Captured Carbon Dioxide. Report prepared by Parsons Brinckerhoff in

collaboration with the Global CCS Institute for the benefit of the Global CCS Institute. Available at: http://hub.globalccsinstitute.com/sites/default/files/publications/14026/accelerating-uptake-ccs-industrial-use-captured-carbon-dioxide.pdf.
Chemical Engineering, 2015. Economic Indicators. http://www.chemengonline.com/economic-indicators-cepci/?printmode=1. (Accessed October 2017).
Chinniyomphanich, U., Wongwanichsin, P., Jitkarnka, S., 2016. SnxOy/SAPO-34 as catalysts for catalytic dehydration of bio-ethanol: impacts of oxidation state, interaction, and loading amount. J. Clean. Prod. 111 (A), 25–33.
Dai, W.L., Luo, S.L., Yin, S.F., Au, T.C., 2009. The direct transformation of carbon dioxide to organic carbonates over heterogeneous catalysts. Appl. Catal. A 366 (1), 2–12.
Dickinson, J., Khan, J., Price, D., Caputo, S.A., Mahnovski, S., Mahnovski Jr., S., 2012. City of New York, Inventory of New York City Greenhouse Gas Emissions. Mayor's Office of Long-Term Planning and Sustainability, New York.
Du, X., Yao, B., Gonzalez-Cortes, S.L., Kuznetsov, V.L., AlMegren, H., Xiao, T., 2015. Catalytic Dehydrogenation of Propane by Carbon Dioxide: a Medium-Temperature Thermochemical Process for Carbon Dioxide Utilisation. Faraday Discuss 183, 161–176.
EIA – US Energy Information Administration, 2015. Petroleum & Other Liquids. www.eia.gov/dnav/pet/hist/LeafHandler.ashx?n=pet&s=ema_epllpa_pin_nus_dpg&f=a. (Accessed February 2015).
Ferreira, H.B.P., Vale, D.L., Andrade, L.S., Mota, C.J.A., Miranda, J.L., 2013. Dimetilcarbonato: Uma Rota para a Conversão de CO_2. Rev. Virtual Quim 5 (2), 188–200.
Firjan, 2015. FIRJAN: Custo da energia elétrica para a indústria da distribuidora Light subirá em média 14,2%. Available at: http://www.firjan.com.br/noticias/firjan-custo-da-energia-eletrica-para-a-industria-da-distribuidora-light-subira-em-media-14-2-1.htm. (Accessed December 2015).
Graaf, G.H., Stamhuis, E.J., Beenackers, A.A.C.M., 1988. Kinetics of low-pressure methanol synthesis. Chem. Eng. Sci. 43 (12), 3185–3195.
He, C., You, F., 2015. Toward more cost-effective and greener chemicals production from shale gas by integrating with bioethanol dehydration: novel process design and simulation-based optimization. AIChE J. 61 (4), 1209–1232.
Huang, C.-H., Tan, C.-S., 2014. A review: CO_2 utilization. Aerosol Air Qual. Res. 14, 480–499.
ICIS, 2008. Chemical Industry News & Chemical Market Intelligence. Indicative Chemical Prices A-z. http://www.icis.com/chemicals/channel-info-chemicals-a-z/. (Accessed November 2008).
ICIS Chemical Business. US chemical profile: Propylene oxide. March 2011. available at: https://www.icis.com/resources/news/2011/03/28/9447303/us-chemical-profile-propylene-oxide/. (accessed: June/2017).
ICIS Chemical Business. ICIS Pricing. Ehylene Glycol. January 2014. https://www.icis.com/globalassets/global/icis/pdfs/sample-reports/chemicals-ethylene-glycol.pdf. (accessed: June/2017).
ICIS Chemical Business. ICIS Pricing. Propylene. January 2014. available at: https://www.icis.com/globalassets/global/icis/pdfs/sample-reports/chemicals-propylene.pdf. (accessed: June/2017).
ICIS Chemical Business. US chemical profile: Propylene oxide. January 2014. https://www.icis.com/globalassets/global/icis/pdfs/sample-reports/chemicals-propylene-oxide.pdf. (accessed: June/2017).
IEA-ETSAP and IRENA, 2013. Production of Bio-etylene Technology Brief I13. http://www.irena.org/publications.
Kawabe, K., 2010. Development of highly selective process for mono-ethylene glycol production from ethylene oxide via ethylene carbonate using phosphonium salt catalyst. Catal. Surv. Asia 14 (3), 111–115.
Li, B., Zhang, L., Song, Y., Bai, D., Jing, H., 2012. Brønsted acid improved cycloaddition of carbon dioxide to propylene oxide. J. Mol. Catal. A Chem. 363–364, 26–30.
Lippe, D.L., 2016. Olefin prices steady despite higher feedstock, production costs. Oil Gas J. 114 (9), 77–81.
Lundin, M.A.B., 2011. Process Integration Study of a Biorefinery Producing Ethylene from Lignocellulosic Feedstock for a Chemical Cluster. Master's Thesis within the Innovative and Sustainable Chemical Engineering Programme. Department of Energy and Environment Division of Heat and Power Technology, Chalmers University of Technology, Göteborg, Sweden. Available at: http://publications.lib.chalmers.se/records/fulltext/140886.pdf.
Matzen, M., Demirel, Yaşar, 2016. Methanol and dimethyl ether from renewable hydrogen and carbon dioxide: alternative fuels production and life-cycle assessment. J. Clean. Prod. 139, 1068–1077.
Methanex Corporation. Available at: https://www.methanex.com/sites/default/files/methanol-price/MxAvgPrice_May%2026%2C%202017.pdf (accessed: June/2017).
Mota, C.J.A., Monteiro, R.S., Maia, E.B.V., Pimentel, A.F., Miranda, J.L., Alves, R.M.B., Coutinho, P.L.A., 2014. O Dióxido de Carbono como Matéria-Prima para a Indútria Química. Produção do Metanol Verde. Rev. Virtual Quim 6 (1), 44–59.
NasaFacts, 2006. Space Shuttle Use of Propellants and Fluids. National Aeronautics and Space Administration. https://www.nasa.gov/centers/kennedy/pdf/167433main_Propellants08.pdf.
Omae, I., 2006. Aspects of carbon dioxide utilization. Catal. Today 115 (1–4), 33–52, 30.
Oncel, S.S., 2017. Green energy engineering: opening a green way for the future. J. Clean. Prod. 142, 3095–3100.
Ong, J., 2014. China MEG to Stay Volatile amid Weak Economy, High Inventory. https://www.icis.com/resources/news/2014/03/18/9763229/china-meg-to-stay-volatile-amid-weak-economy-high-inventory/.
Otto, A., Grube, T., Schiebahn, S., Stolten, D., 2015. Closing the loop: captured CO_2 as a feedstock in the chemical industry. Energ & Environ Sci 8 (11), 3283–3297.
O'Hare, J., Cope, E., Warde, S., 2015. Five Steps to Eco Design. Improving the Environmental Performance of Products through Design. Available at: http://www.grantadesign.com/download/pdf/FiveStepsToEcoDesign.pdf. (Accessed 20 March 2017).
Pina, E.A., Palacios-Bereche, R., Chavez-Rodriguez, M.F., Ensinas, A.V., Modesto, M., Nebra, S.A., 2015. Reduction of Process Steam Demand and Water-usage through Heat Integration in Sugar and Ethanol Production from Sugarcane - Evaluation of Different Plant Configurations Energy. https://doi.org/10.1016/j.energy.2015.06.054.
Poliakoff, M., Leitner, W., Streng, E.S., 2015. The twelve principles of CO_2 chemistry. Faraday Discuss. 2015 (183), 9–17.
Rodrigues, J.A.R., 2011. Do engenho à biorrefinaria. A Usina de Açúcar como Empreendimento Industrial para a Geração de Produtos Bioquímicos e Biocombustíveis. Quím. Nova 34 (7), 1242–1254.
Ruiz-Mercado, G.J., Gonzalez, M.A., Smith, R.L., 2013. Sustainability indicators for chemical processes: III. Biodiesel case study. Ind. Eng. Chem. Res. 52, 6747–6760.
Sakakura, T., Choi, J., Yasuda, H., 2007. Transformation of carbon dioxide. National Institute of advanced industrial science and technology (AIST). Chem. Rev. 107, 2365–2387.
Sengupta, D., Pike, R.W., 2013. Chemicals from Biomass: Integrating Bioprocesses into Chemical Production Complexes for Sustainable Development. CRC Press, Taylor & Francis Group, Boca Raton, FL.
Song, C., 2006. Global challenges and strategies for control, conversion and utilization of CO_2 for sustainable development involving energy, catalysis, adsorption and chemical processing. Catal. Today 115, 2–32.
Takahara, I., Chang, W.C., Mimura, N., Saito, M., 1998. Promoting effects of CO2 on dehydrogenation of propane over a SiO2-supported Cr2O3 catalyst", advances in chemical conversions for mitigating carbon dioxide. Stud. Surf. Sci. Catal. 114, 419–422.
Tecnon Orbichem, 1 November 2013. Chem-net FACTS. Ethylen Oxide. Available at: http://www.orbichem.com/userfiles/CNF%20Samples/eox_13_11.pdf. (Accessed June 2017).
Tsiropoulos, I., Faaij, A.P.C., Lundquist, L., Schenker, U., Briois, J.F., Patel, M.K., 2015. Life cycle impact assessment of bio-based plastics from sugarcane. J. Clean. Prod. 90, 114–127.
Turton, R., Bailie, R.C., Whiting, W.B., Shaeiwitz, J.A., Bhattacharyya, D., 2012. Analysis, Synthesis, and Design of Chemical Processes, fourth ed. Prentice Hall, Michigan, USA. ISBN-13: 978-0-13-261812-0.
UDOP - União dos Produtores de Bionergia, 2015. http://www.udop.com.br/index.php?item=alcool (accessed: February/2015).
Van-Dal, E.S., Bouallou, C., 2013. Design and simulation of a methanol production plant from CO_2 hydrogenation. J. Clean. Prod. 57, 38–45.
Wiesberg, I.L., de Medeiros, J.L., Alves, R.M.B., Coutinho, P.L.A., Araújo, O.Q.F., 2016. Carbon dioxide management by chemical conversion to methanol: HYDROGENATION and bi-reforming. Energy Convers. Manag. 125, 320–335. https://doi.org/10.1016/j.enconman.2016.04.041.
Wu, G., Wang, Y., Wang, L., Feng, W., Shi, H., Lin, Y., Zhang, T., Jin, X., Wang, S., Wu, X., Yao, P., 2013. Epoxidation of propylene with H2O2 catalyzed by supported TS-1 catalyst in a fixed-bed reactor: experiments and kinetics. Chem. Eng. J. 215–216, 306–314.